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PITTSBURGH ATOMIC SCIENCES INSTITUTE

TECHNICAL PROGRESS SUMMARY NO. 21

rept.

ORDER NUMBER:

The Advanced Research Projects Agency
ARPA Order No. 2686

CONTRACT NUMBER:

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N00014-76-C-0098

PROGRAM CODE NUMBER:

✓ ARPA Order-2686
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NAME OF CONTRACTOR:

Departments of Physics and Chemistry
University of Pittsburgh
Pittsburgh, Pennsylvania 15260

DATE OF CONTRACT:

July 1, 1975

EXPIRATION DATE:

September 30, 1977

AMOUNT OF CONTRACT:

\$335,000

PROJECT SCIENTISTS:

10
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Professor of Physics

Telephone: Area Code 412
624-4354

SCIENTIFIC OFFICER:

6
Code N00014

TITLE OF WORK:

ATOMIC AND MOLECULAR PROCESSES

DISTRIBUTION STATEMENT A

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Pittsburgh Atomic Sciences Institute

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Graduate Research Assistants:

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Sheng L. Lin
Yueh Jaw Shiu

Visiting Faculty:

None

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TECHNICAL PROGRESS REPORT NO. 21

Pittsburgh Atomic Sciences Institute

University of Pittsburgh

Pittsburgh, Pa. 15260

I. Summary of Research

Since the present semi-annual progress report spans three months of work (April - June, 1976) under the previous contract N00014-76-C-0098 as well as three months under the present contract (July - Sept. 1976) topics of investigation from both contracts are discussed and, as usual, are identified by title, senior investigator(s) in charge of the work, and the general program to which they belong.

A. Laser Physics1. Energy Transfer Processes of Laser Interest (F. Kaufman and E. C. Zipf)a. F. Kaufman's Group:

Much further work was done on the formation of vibrationally highly excited molecules in their initial, unrelaxed energy distribution and on their subsequent collisional relaxation. This work utilizes highly sensitive detection of infrared chemiluminescence with moderate spectral resolution in a fast flow system ($\sim 10^4$ cm sec⁻¹ velocity) with large excess of helium carrier gas (10^4 to 10^5 fold).

Good progress was achieved in three areas:

(1) Improved initial distributions of HCl^\dagger arising from $\text{H} + \text{Cl}_2$ and $\text{H} + \text{CINO}$ were obtained by doing simultaneous least squares computer fits of both the fundamental and first overtone band envelopes. The following relative vibrational level populations were obtained for $\text{H} + \text{Cl}_2$, where the first entry for each level is our result, the second that of

Polanyi's group, and the third that of Setser's: (normalized to $v = 2$)

$v = 1$: 0.33, 0.28, 0.32 ;	$v = 2$: 1.0, 1.0, 1.0 ;
$v = 3$: 1.01, 0.92, 0.77 ;	$v = 4$: 0.22, 0.1, < 0.15 ;
$v = 5$: 0.014, -, < 0.045 .	

It seems clear that in spite of the much higher pressure of our experiments (~ 1 Torr) the level distribution is somewhat less relaxed than that reported elsewhere. For $H + C_2NO$ a similar comparison with Polanyi's group and with a French group (Menard-Bourcin et al.) gives the following results: (normalized to $v = 5$)

$v = 1$: 0.12, -, 0.18 ;	$v = 2$: 0.24, -, 0.32 ;
$v = 3$: 0.49, 0.82, 0.50 ;	$v = 4$: 0.88, 0.96, 0.46 ;
$v = 5$: 1.0, 1.0, 1.0 ;	$v = 6$: 0.50, 0.48, - ;
$v = 7$: 0.11, 0.10, - .	

Our distribution is again less relaxed than that of the others.

(2) The collisional relaxation processes are now studied in two ways: either by injecting the molecular reactant (Cl_2 , C_2NO) at the edge of the field of view in the presence or absence of added quencher and plotting ratios of observed level densities vs. quencher concentrations, or by moving the injector to various upstream positions and thereby mapping out the time histories of all vibrational levels in detail. In order to extract consistent quenching rate constants from such plots a non-linear least squares computer program was written which simultaneously fits all such points to the integrated, coupled rate expression for all levels using known A-values and assuming that quenching occurs only by $\Delta v = 1$ steps. One also needs information on the surface removal rate of the excited species and this term is introduced in parametric form

corresponding to a range of fairly high (i.e. efficient) wall relaxation probabilities. Early attempts to use this method to determine quenching rate constants of $\text{C}\lambda\text{NO}$ for HCl^\dagger gave extremely high values, in the 2 to $6 \times 10^{-10} \text{ cm}^3 \text{ sec}^{-1}$ range, i.e. near unit probability per collision. For added CO_2 , more reasonable values of 0.8 to $8 \times 10^{-11} \text{ cm}^3 \text{ sec}^{-1}$ were obtained. It has been a weakness of the experimental method that the small H-atom concentrations produced in the modulated microwave discharge have been measured only very approximately by the intensity of the chemiluminescence with increasing amounts of second reactant. This has led us to modify the apparatus as follows:

(3) The discharge section was moved farther upstream along an added secondary flow tube of smaller diameter, i.e. at higher pressure through which a small fraction of the total flow passes. The H-atom concentrations are thereby one to two orders of magnitude higher than in the larger flow tube downstream and they can be "titrated" using another reaction, $\text{H} + \text{NO}_2 \rightarrow \text{OH} + \text{NO}$, while being monitored downstream by the HCl^\dagger chemiluminescence at different wavelengths. Care must be taken, of course, not to degrade the square wave modulation of the atom stream by this additional passage. Early experiments indicated that about 30% of the H_2 was dissociated in the discharge at about 200 fold dilution with He. The quenching experiments are now being completed and written up, and other systems, including V-E transfer reactions are to be studied soon.

b. E. C. Zipf's Group

An extensive series of measurements has been carried out investigating the collisional deactivation of the metastable $\text{N}_2(\text{A}^3\Sigma_u^+)$ state by a variety of molecular and atomic targets with particular emphasis on the radiating states excited by this process. This includes the population of the very

important $O(^1S)$ state by the process $N_2(A) + O(^3P) \rightarrow O(^1S) + N_2$. Time-of-flight [TOF] techniques have been used in some of these studies because they permit a direct measurement of the pertinent collision cross section and then the calculation of the reaction rate coefficient over a large kinetic temperature range (in excess of $10^5 K$) - a measurement not feasible by conventional chemical techniques. These hot atom/molecule studies also permit us to study energy transfer processes leading to photon excitation not observed under equilibrium conditions and to observe the collisional deactivation of short-lived "pseudo" metastable species that are very important in high-pressure discharges and arcs. Additional experiments are now in progress involving other metastable species and a variety of high-mass polyatomic molecules as source and quenching gases.

2. Electron-Ion and Ion-Ion Recombination under Laser Plasma Conditions

(M. A. Biondi and E. C. Zipf)

a. M. A. Biondi's Group

The studies of the dissociative recombination of Xe_2^+ and electrons to form various Xe^+ excited states have been completed. It is found that the data can be fitted within $\pm 15\%$ by a single-term power law dependence of the form $\alpha(\text{cm}^3/\text{sec}) = 2.66 \times 10^{-7} [300/T_e(K)]^{0.60}$ over the range $300 K < T_e < 8000 K$, although a smooth transition from a $T_e^{-1/3}$ variation between 300 K and 700 K to a $T_e^{-0.72}$ variation between 1300 K and 7400 K provides a more accurate fit.

At $T_e = 300 K$ (thermal electrons) the Xe^* excited states formed lie at energies up to but not exceeding the position of the Xe_2^+ ground electronic and vibrational state, some 1.0 eV below the Xe^+ ($^2P_{3/2}$) ion ground state. Excited states belonging to both the $^2P_{3/2}$ and $^2P_{1/2}$ ion

core states are observed. With electron heating to ~ 8000 K additional Xe^* excited states are formed, some lying as much as ~ 0.8 eV above the position of the Xe_2^+ ion ground state, and again excited states belonging to both the $^2\text{P}_{3/2}$ and $^2\text{P}_{1/2}$ ion core are observed. These observations are consistent with dissociative recombination between plasma electrons and ground state Xe_2^+ ions to form all energetically allowed Xe^* excited states. Radiative cascading to lower levels should then rapidly lead to production of metastable and resonance level ($6s$ and $6s'$) excited xenon atoms.

b. E. C. Zipf's Group

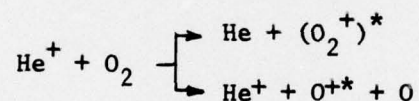
The dissociative recombination of CO_2^+ , N_2O^+ , and NO_2^+ ions in both thermal equilibrium and vibrationally hot is under active study. Vibrationally excited polyatomic ions have been found to produce highly selective excitation of near UV radiation with impressive efficiencies. A technique has been developed to heat these ions specifically and to study the unusual UV emission spectra produced by these excited ions. The spectroscopic data obtained in these studies complements similar information developed in our dissociative excitation and time-of-flight experiments (Task 4) which, when combined, provide unusual insights into the quantum mechanical details of molecular dissociation and lay the foundation for exploiting these processes for laser applications.

3. Atomic Ion-Molecule Charge Transfer Processes (M. A. Biondi)

The goal of this program is to develop an empirical means of predicting, a priori, whether a charge transfer process between a given atomic or molecular ion and a particular molecule (leading to excited state formation) will be fast or slow. We have found experimentally

that a number of such reactions appear to be governed by the following principle: Given a reaction of the form $A^+ + BC \rightarrow A + (BC^+)^*$. Then, using the undistorted potential curves for the molecular states, BC and $(BC^+)^*$, if a vertical Franck-Condon transition between initial and final molecular states makes the charge transfer nearly energy resonant (slightly exoergic), the reaction to produce that state will be fast; if not, the reaction is slow. Examples of charge transfer reactions which we have found to obey this principle are: $He^+ + H_2$, $He^+ + N_2$, $He_2^+ + N_2$, $O^+ + O_2$, $O^+ + NO$.

Our previous studies had indicated that an additional fast reaction,



also led to substantial $(O_2^+)^*$ formation; however other experiments disagreed with our results. We have now redetermined the branching ratio of this reaction at thermal energy and find very little O_2^+ formed; only O^+ is detected. (The earlier work was evidently falsified by O_2^+ production by O^{+*} , since unexcited O^+ ions react very slowly with O_2 and would not have affected our results through a secondary reaction.)

Thus, having found an apparent exception to above-stated empirical principle governing molecular excited state formation by non-resonant charge transfer, we are reconsidering the problem.

4. Dissociative Excitation of Molecules by Electron Impact (E. C. Zipf)

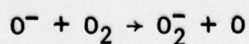
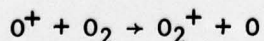
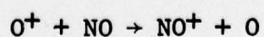
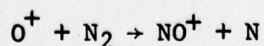
The dissociative excitation of N_2O , NO_2 , CH_4 , CD_4 , NH_3 , ND_3 , D_2 , HD , and H_2 have been studied in our time-of-flight [TOF] apparatus and a variety of excited Rydberg and metastable states have been identified.

The threshold energies and excitation functions for the principal

dissociation channels have been obtained. The absolute magnitudes of the electron-impact excitation cross sections for many of these processes have also been estimated. In a separate series of studies involving a different experimental facility the near ultraviolet ($4000\text{\AA} - 2000\text{\AA}$) and vacuum ultraviolet ($2000\text{\AA} - 400\text{\AA}$) flux produced by these processes have also been explored in a preliminary way. Complementary visible and near - IR ($4000 - 8000\text{\AA}$) studies have also been carried out. The optical and [TOF] data when combined provide very detailed insights into the general mechanism of molecular dissociation. In particular the virtues and limitations of the core-ion model of dissociative excitation have been placed in clearer perspective. The optical studies have included a variety of complex hydrocarbon molecules with large molecular weights as well as the more conventional target gases mentioned above.

5. Theoretical Calculation of V→E Transfer Reactions, Excimer Curves and Electron Excitation of Atoms and Molecules (J. N. Bardsley)

The development of our facility for the simulation of ion motion in uniform electric fields has been concluded. We have computed the speed distributions for O^+ , O^- , H^- , Li^+ and K^+ in He and for O^+ and K^+ in Ar and have analyzed the mobilities of these systems in terms of the interatomic potentials. These distributions have permitted us to analyze the drift tube measurements of the reactions



Although the Monte-Carlo programs are available for further analysis, our activity in this area will be significantly reduced.

The pseudopotential program has been developed through our collaboration with W. J. Stevens on the study of the dimers Mg_2 and Hg_2 . It has been shown that the replacement of the ab initio treatment of the Mg atom core by a pseudopotential does not distort the valence orbitals and indeed permits a more accurate treatment of core polarization. Further calculations on Na_2 are anticipated, due to the interest of Shuker and Phelps in dissociative recombination of Na_2^+ .

The model potential approach has been extended to include relativistic effects through the solution of the Dirac equation for the valence electrons. In collaboration with D. W. Norcross we have computed wave functions and oscillator strengths for the thallium atom. These results have formed the basis of the analysis of electron impact excitation of thallium by Gallagher and his colleagues. Calculations of this type for other type III metals are under consideration.

The recent beam experiments by McGowan et al. on dissociative recombination together with the data from this Institute on cluster ions suggest that there cannot be a clear distinction between the direct and indirect modes of this process and that the indirect process may be especially important for cluster ions. We have initiated a reexamination of these processes.

B. Optics

1. Particulate Technology (W. L. Fite)

The activity regarding detection of particulates in the stratosphere has been concerned primarily with the design of an improved flight package to go onto balloon parachute experiments. Having used the prototype

package in three flights, a number of obvious improvements of a minor nature became evident and some of a fairly major nature as well.

The major item has been the development of a circuit to maintain the temperature of the hot surface at which particulates decompose constant irrespective of changes in pressure and changes in speed through the ambient air as the parachute descends. In the original package, the surface temperature was held constant by regulation of the electrical resistance of the hot filament, i.e., if the cooling increased during fall more power would be provided to the filament until its initial resistance value was restored. In the new flight package, the hot surface temperature will be regulated by the brightness of the surface, with the thermal radiation from the surface being detected by an in situ photoresistive cell. The circuitry has been proven in the breadboard form, and parts for the new flight package are on order. We anticipate delivery within the next month to six weeks of all components, after which we shall try to get on board additional balloon-parachute flights, probably with Dr. Anderson of the Michigan group.

II. Publications and Technical Presentations

A. Publications

Symmetric Charge Transfer in Low-Energy Ion-Atom Collisions, S. Sinha and J. N. Bardsley, Phys. Rev. A14, 104 (1976).

Monte Carlo Simulation of Ion Motion in Drift Tubes, S. L. Lin and J. N. Bardsley, submitted to J. Chem. Phys. for publication.

Measurement of Ortho-Para Ratio in Gas Phase Hydrogen Atom Recombination, L. P. Walkauskas and F. Kaufman, J. Chem. Phys. 64, No. 9, 1976.

Flowing Afterglow Studies of Hydronium Ion Clustering Including Diffusion Effects, V. M. Bierbaum, M. F. Golde and F. Kaufman, accepted J. Chem. Phys.

Translational Spectroscopy of Metastable Fragments Produced by Dissociative Excitation of Atmospheric Gases by Electron Impact. I. Nitrogen, W. C. Wells, W. L. Borst and E. C. Zipf, Phys. Rev. A14, 695, 1976.

Translational Spectroscopy of Metastable Fragments Produced by Dissociative Excitation of Chlorine, W. C. Wells and E. C. Zipf, submitted to Journal of Chemical Physics.

Translational Spectroscopy of Metastable Fragments Produced by Dissociative Excitation of Oxygen by Electron Impact: Comparison of Time-of-Flight Spectra, W. C. Wells and E. C. Zipf, submitted to Journal of Chemical Physics.

A Low Voltage, High Current Electron Gun, P. Erdman and E. C. Zipf, submitted to Review of Scientific Instruments.

B. Technical Presentations

Stratospheric Chemistry, NO₂ Fluorescence, and the Apollo-Soyuz Ultraviolet Absorption Experiment, seminar, Stanford Research Institute, Menlo Park, CA, September 1976, Frederick Kaufman.

Deliberations and Findings of the Atmospheric Chemistry Panel of the National Academy of Sciences, invited paper, International Conference on the Stratosphere and Related Problems, Utah State University, Logan, Utah, September 1976, Frederick Kaufman.

C. Other Activities Relating to ARPA

J. N. Bardsley and S. L. Lin participated in a symposium on ion-molecule reactions in drift tubes on April 25th in Washington, D. C.

M. A. Biondi and F. Kaufman attended the Electronic Transition Laser Conference at Snowmass, Colorado, September 6-10, 1976.

Frederick Kaufman attended meetings of the Atmospheric Chemistry Panel and of the Committee on Impacts of Stratospheric Change in Washington, D. C. on April 10, in Boulder, Colorado on April 27 and 28, in Washington, D. C. on July 26 and 27, August 22 and 23, and September 13, 1976.

Frederick Kaufman attended an Advisory Board meeting of the Office of Chemistry and Chemical Technology of the National Academy of Sciences in Washington, D. C. on April 24, 1976.

Frederick Kaufman visited the ARPA office in Washington, D. C. for discussion with Major Canavan on May 20.

Frederick Kaufman attended the semi-annual meeting of the AFOSR Chemistry Panel at Georgetown University in Washington, D. C. on May 21.

III. Visiting Scientists

H. Narumi, Hiroshima University (August 1976)

E. Arijs, Institute for Space Sciences, Belgium

F. M. Page, University of Aston in Birmingham, England

M. Koslin, Rensselaer Polytechnic Institute

D. Smith, University of Birmingham

R. S. Narcisi, Air Force Cambridge Laboratories

IV. Degrees Awarded

Byron Carnahan, Ph.D., October 1976

Sheng L. Lin, Ph.D., September 1976

J. J. Margitan, Ph.D., September 1976

Senior InvestigatorEst. Funds Expended and Committed (Thousands)

J. N. Bardsley	\$ 15.4
M. A. Biondi	60.0
W. L. Fite	38.6
F. Kaufman	48.0
E. C. Zipf	<u>10.0</u>
Total Expended and Committed	172.0
Available Funds	<u>175.0</u>
Estimated Funds Remaining as of 9/30/76	3.0

University Accounting of Funds

Expended as of 9/30/76	168.9
Available Funds	<u>175.0</u>
Remaining Funds as of 9/30/76	6.1